

Coles, S.J., Holmes, R., Hursthouse, M.B., and Price, D.J. (2002)  
Biphenyl-3,3',5,5'-tetracarboxylic acid. Acta Crystallographica. Section  
E: Structure Reports Online, 58 (6). o626-o628. ISSN 1600-5368

<http://eprints.gla.ac.uk/12748>

Deposited on: 4 October 2012

## Biphenyl-3,3',5,5'-tetracarboxylic acid

Simon J. Coles,\* Richard Holmes,  
Michael B. Hursthouse and  
Daniel J. Price

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, England

Correspondence e-mail: s.j.coles@soton.ac.uk

## Key indicators

Single-crystal X-ray study

$T = 120\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

$R$  factor = 0.067

$wR$  factor = 0.203

Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of biphenyl-3,3',5,5'-tetracarboxylic acid,  $\text{C}_{16}\text{H}_{10}\text{O}_8$ , forms a supramolecular assembly of three interpenetrating corrugated sheets.

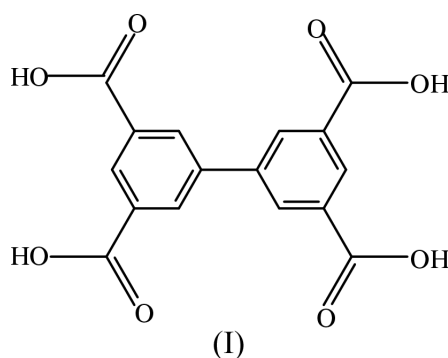
Received 12 April 2002

Accepted 3 May 2002

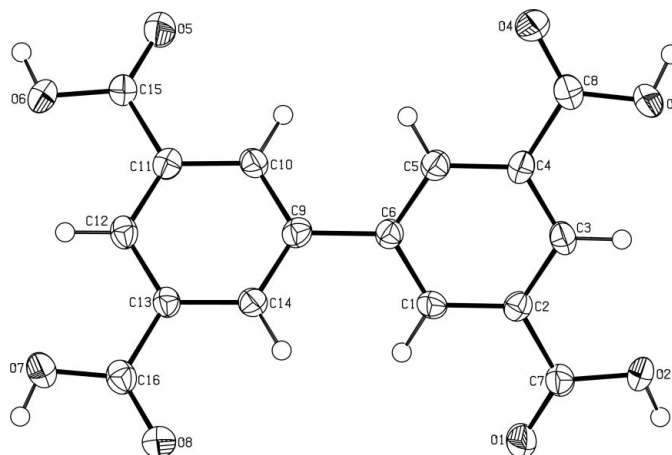
Online 17 May 2002

## Comment

The title compound, (I), is composed of two essentially planar benzene-3,5-dicarboxylic acid groups that are orientated at a dihedral angle of  $40.66(7)^\circ$  with respect to each other (Fig. 1). The bond lengths and angles in the molecule are in accordance with standard values (Orpen *et al.*, 1992) derived from the Cambridge Structural Database (CSD; Allen & Kennard, 1993).



All four of the carboxylic acid groups in (I) form the classic cyclic  $R_2^2(8)$  hydrogen-bond motif (Etter *et al.*, 1990) with the acid groups of neighbouring molecules (Table 1). These interactions result in a two-dimensional sheet with a  $4^4$  network topology (Fig. 2). While the carboxylic acid groups are essentially coplanar with their respective phenyl rings, the



**Figure 1**  
View of (I) (50% probability displacement ellipsoids).

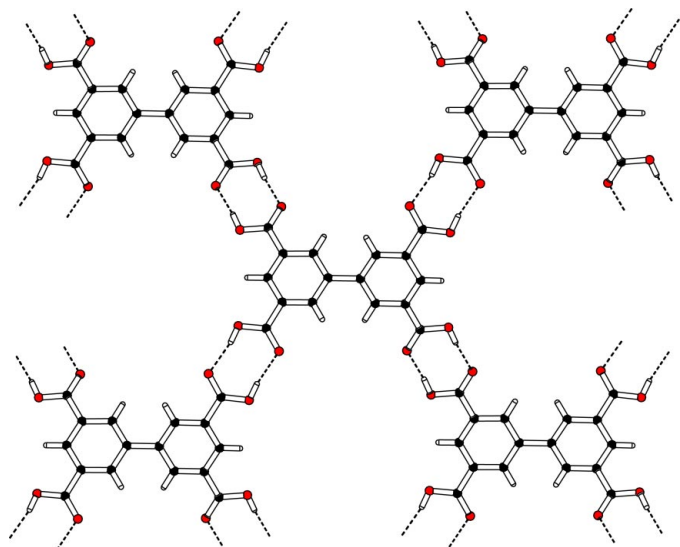


Figure 2

View down the *b* axis, showing the two-dimensional hydrogen-bonded network of (I).

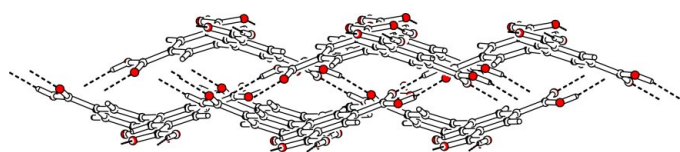


Figure 3

View down the *c* axis of the interpenetrating corrugated sheets that comprise the crystal structure of (I).

twist in the central C—C bond results in a corrugated structure. Thus, the supramolecular structure of this material comprises three, mutually interwoven, corrugated sheets (Fig. 3).

The structure of (I) compares well with other highly symmetric benzene polycarboxylic acids. In these molecules, where strong and predictable hydrogen bonding determines the network topology, there is a clear relationship between the molecular symmetry (the number of acid groups) and the two-dimensional network formed by the tessellation of these flat molecules. For example, the benzenedicarboxylic acids all form one-dimensional hydrogen-bonded ribbons (CSD refcode PHTHAC: Nowacki & Jaggi, 1957; BENZDC01: Alcala & Martínez-Carrera, 1972; TEPHTH: Bailey & Brown, 1967). 1,3,5-Benzenetricarboxylic acid (BTHOAC; Duchamp & Marsh, 1969) forms a  $6^3$  two-dimensional network, whilst 1,2,3,4,5,6-benzenhexacarboxylic acid (MELLIT; Darlow, 1961) forms a  $3^6$  two-dimensional net. The 1,3,5-benzenetricarboxylic acid shows further similarity with (I), in that the two-dimensional network contains very large hexagonal cavities, through which nine separate sheets interpenetrate in a supramolecular fashion, to yield a three-dimensional interwoven structure.

## Experimental

Biphenyl-3,3',5,5'-tetracarboxylic acid, (I) (Burton & Kenner, 1923), was, in this case, synthesized by a two-step procedure. 5-Iodo-*m*-

xylene (6.00 g, 25 mmol) and copper powder (2.46 g, 38 mmol) were heated to 503 K under autogenous pressure for 50 h. The solid copper residues were removed by filtration and the coupled product, 3,3',5,5'-tetramethylbiphenyl, was purified by column chromatography (hexane/silica) (0.98 g, 37%). A suspension of 3,3',5,5'-tetramethylbiphenyl (0.6 g, 2.9 mmol) in water (125 ml) was treated with  $\text{KMnO}_4$  (3.6 g, 22.8 mmol) and heated under reflux for 100 h. Filtration, followed by acidification with aqueous HCl, afforded the tetracarboxylic acid (0.28 g, 30%), which was recrystallized under hydrothermal conditions on cooling from 503 K.

## Crystal data

$\text{C}_{16}\text{H}_{10}\text{O}_8$   
 $M_r = 330.24$   
 Monoclinic,  $P2_1/c$   
 $a = 8.1662$  (7) Å  
 $b = 14.3524$  (14) Å  
 $c = 12.093$  (1) Å  
 $\beta = 109.590$  (4)°  
 $V = 1335.3$  (2) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.643$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 19 752 reflections  
 $\theta = 1\text{--}27.5^\circ$   
 $\mu = 0.14$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Block, colourless  
 $0.16 \times 0.14 \times 0.05$  mm

## Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SORTAV; Blessing, 1997)  
 $T_{\min} = 0.979$ ,  $T_{\max} = 0.993$   
 16 495 measured reflections  
 2965 independent reflections

1309 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.122$   
 $\theta_{\max} = 27.4^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -18 \rightarrow 18$   
 $l = -15 \rightarrow 15$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.067$   
 $wR(F^2) = 0.203$   
 $S = 0.98$   
 2965 reflections  
 221 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0991P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.29$  e Å<sup>-3</sup>

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O5 <sup>i</sup>	0.84	1.80	2.631 (3)	173
O3—H3A...O8 <sup>ii</sup>	0.84	1.84	2.656 (3)	165
O6—H6...O1 <sup>iii</sup>	0.84	1.81	2.637 (3)	168
O7—H7...O4 <sup>iv</sup>	0.84	1.82	2.650 (3)	170

Symmetry codes: (i)  $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$ ; (ii)  $1 + x, y, 1 + z$ ; (iii)  $1 + x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iv)  $x - 1, y, z - 1$ .

H atoms were constrained to idealized positions, with their displacement parameters riding on the values of their parent atoms.

Cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

The authors thank the EPSRC for funding of crystallographic facilities and an Advanced Research Fellowship to DJP.

## References

- Alcala, R. & Martínez-Carrera, S. (1972). *Acta Cryst.* **B28**, 1671–1677.
- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

- Bailey, M. & Brown, C. J. (1967). *Acta Cryst.* **22**, 387–391.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–429.
- Burton, H. & Kenner, J. (1923). *J. Chem. Soc.* pp. 1043–1045.
- Darlow, S. F. (1961). *Acta Cryst.* **14**, 159–166.
- Duchamp, D. J. & Marsh, R. E. (1969). *Acta Cryst.* **B25**, 5–19.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Nowacki, W. & Jaggi, H. (1957). *Z. Kristallogr.* **109**, 272–276.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G., & Taylor, R. (1992). *International Tables for Crystallography*, Vol. C. Dordrecht: Kluwer Academic Publishers.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.